

SPECTROELECTROCHEMICAL SENSOR FOR TECHNETIUM; PRECONCENTRATION AND QUANTIFICATION OF TECHNETIUM IN POLYMER MODIFIED ELECTRODES

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INTRODUCTION

One of the goals of the Environmental Management Sciences Program is to support basic research addressing fundamental issues that may be critical to advancing the remediation of Department of Energy (DOE) sites nationwide. One critical area of this remediation is the need to monitor radiochemical constituents in various areas, ranging from the containment of low and high-level radioactive waste to monitoring of contaminant plumes in subsurface water. Current methods of analysis are time consuming and hazardous at best, requiring lengthy sampling, preparation, analysis, and data interpretation. A better approach would be to use sensors to perform rapid, sensitive, and economic *in situ* analysis for various constituents of interest.

Technetium (Tc) is one such constituent of radioactive waste where the need for a chemical means of detection exists, but a sensor does not. Technetium is not found in appreciable quantities in nature; however, the isotope ⁹⁹Tc is a byproduct of the thermal nuclear fission of ²³⁵U, ²³³U, and ²³⁹Pu at 6.1 %, 4.8 %, and 5.9 % yields respectively¹, and significant quantities of ⁹⁹Tc exist at many DOE sites. Technetium 99 exhibits rather weak radiological β^- decay ($E_{\max} = 0.292$ keV) but it is of particular concern for two reasons: its long half life (2.13×10^5 yrs) and high solubility of its most common form in environmental conditions, pertechnetate (TcO_4^-).² Pertechnetate does not readily adsorb to most minerals, and therefore in aqueous form and under suitable conditions, it may rapidly present itself to subsurface waters.^{3, 4}

The goal of our current EMSP funded research has been to develop a sensor for Tc, capable of exceeding the EPA's 900 pCi/L ($\sim 5 \times 10^{-10}$ M) standard for drinking water. Our previous research has focused on a novel sensing technology combining three modes of selectivity (electrochemistry, spectrophotometry, and selective partitioning) into a single sensing technique, spectroelectrochemistry. We have demonstrated that spectroelectrochemistry performed using ion-exchange-polymer-doped films coated on waveguides with optically transparent electrodes (OTE) provides a unique opportunity to detect analytes in the presence of interferences.⁵ The ability of the ion-exchange-polymer-doped film to perform charge exclusion while increasing the concentration of the target analyte near the electrode surface combined with electrochemical excitation and spectrophotometric quantification provides a model strategy for the detection of many analytes.

In the work presented here, we demonstrate the ability to preconcentrate pertechnetate in thin films doped with poly(dimethyldiallylammonium chloride) (PDMDAAC), poly(vinylbenzyltrimethyl-ammonium chloride) (PVTAC), quarternized poly(4-vinylpyridine) (QPVP) at the surface of a waveguide with an optically transparent electrode. The change in optical absorbance due to electrochemical deposition of TcO_2 in the anion-exchange film is demonstrated as a simple method to produce a spectroelectrochemical determination of technetium concentration, and verify these results via radiochemical dose rate.

MATERIALS AND METHODS

Caution: Technetium 99 is a known beta emitter ($E_{\text{max}} = 0.292 \text{ keV}$) with a half life of $2.13 \times 10^5 \text{ yr}$. Amounts of ^{99}Tc in greater than 20 mg may cause secondary X-rays produced by the action of the β^- rays on glass (Brehmstrahlung). All experiments described herein were performed at Pacific Northwest National Laboratory in the Radiochemical Processing Laboratory, a DOE Hazard Category II Non-reactor Nuclear Facility by a properly equipped analyst with Radiological Worker II Certification.

Chemicals and Reagents: A pertechnetate stock solution was prepared and used at Pacific Northwest National Laboratory by dissolving 1.5703 g of ^{99}Tc in 100 mL of 2 M HNO_3 . The activity was measured to be $5.95 \times 10^8 \text{ dpm/mL}$. Poly(diallyldimethylammonium chloride) solution containing 20 wt % solution in water was obtained from Polysciences. Poly(4-vinylpyridine) (MW), polyvinyl alcohol (MW 85,000-146,000, 98-99 % hydrolyzed), tetraethyl orthosilicate (99.999 %), and 3-aminopropyltriethoxysilane were purchased from Aldrich. Poly(vinylbenzyltrimethylammonium chloride) (MW 400,000) solution containing 30 wt % in water was obtained from Scientific Polymer Products. Stock solutions for polymer blends were prepared either by dilution of commercial solutions or by dissolution of solid polymer in deionized water from a Barnstead water purification system. All the other compounds (ACS-certified Reagent Grade) were used without further purification.

Apparatus: Electrochemistry for pertechnetate experiments was performed with a remotely operable potentiostat, designed in our laboratory.⁶ All potential values were measured vs. Ag/AgCl reference electrode (Cypress Systems, 3M KCl). Indium tin oxide (ITO) coated glass (Corning 1737F and 7059, 11-50 $\Omega/\text{sq.}$, 150 nm thick film on 1.14 mm glass) was purchased from Thin Film Devices and was cut into 1 cm x 4.5 cm slides and used as the working electrode. For thin film electrochemistry, a special cell was designed which employed a large-area platinum coated titanium mesh as the counter electrode. Spectrophotometry for technetium experiments was performed using a Hewlett-Packard Diode Array Spectrophotometer. Radiochemical dose rate measurements were performed using a vacuum-tube ionization chamber, commonly called a cutie-pie (CP).

Thin Film Preparation: Silica sols were prepared according to a previously reported protocol.⁷ Incorporation of PDMDAAC and QPVP into the silica sol was performed by mechanically blending the polyelectrolyte solution with the silica sol just prior to spin-

coating. Preparation of the PVA-PVTAC films was performed following a procedure previously described.⁸ In all cases, the mixture of polymer and matrix was spin-coated to desired thickness on the surface of ITO coated slides with a Headway photo resist spinner operated at 3000 rpm. QPVP was prepared starting from PVP by dissolving 0.5g PVP in 50 mL Methanol in a roundbottom flask, to which is added 1mL CH₃I (Fisher, 99.8%) and some glass beads. The solution is refluxed for 6 h (heating mantle, condenser). The solution goes from clear to a cloudy yellow. Several portions (~25 mL each) of diethyl ether are added to complete precipitation and decanted after the product has settled for a couple hours, to remove some of the solvent and also remove unwanted organics [byproducts, contaminants, etc]. The remaining solvent is evaporated on a rotovap. The QPVP-iodide salt is weighed, and dissolved in DI water sufficient to make 20% solution (weight/volume). 0.1g AgNO₃ is added for each milliliter of QPVP solution to remove iodide counter ions by precipitation of AgI and replace them with nitrate counter ions. The solution is centrifuged (15,000 rpm, 15 min, several times) to remove solid AgI. KCl (5-10 grains/crystals) is then added to precipitate out excess silver, and the solution is centrifuged again to remove AgCl. This process is repeated until the addition of KCl does not cause precipitation of AgI to occur. Failure to remove all excess silver results in poor film quality.

RESULTS AND DISCUSSION

The electrochemistry of TcO₄⁻ was investigated at ITO because this is the OTE that has worked so well for our spectroelectrochemical sensors. Voltammograms at bare ITO gave a poorly defined reduction wave for TcO₄⁻ and complicated electrochemistry analogous to that reported by Mazzocchin et al. on platinum. A representative voltammogram is shown in Figure 1 with electrode reactions assigned by Mazzocchin et al.⁹ An important observation is that TcO₄⁻ is reducible to lower oxidation states on ITO, which is a key step in developing the spectroelectrochemical sensor for TcO₄⁻. The electrochemistry of TcO₄⁻ was then investigated at ITO coated with anion exchange films to determine if TcO₄⁻ is preconcentrated from solution into the sensing film, which is another key step in the sensor concept. Since TcO₄⁻ is anionic, tests were run on three anion exchange films that we have developed and used successfully to preconcentrate other anions: PVA-PVTAC, PDMDAAC-SiO₂, and QPVP-SiO₂. Voltammograms of TcO₄⁻ (Figure 2) showed a much more sharply defined reduction wave at all three films tested.

Four features of the voltammograms are important. First, the current for the reduction wave of TcO₄⁻ (at about -1100 mV) is considerably larger at all of the film-coated ITOs compared to bare ITO, which is indicative of a preconcentration of TcO₄⁻ into all of the films. Second, there are differences in the enhancement of TcO₄⁻ reduction wave potential by the three films, even though

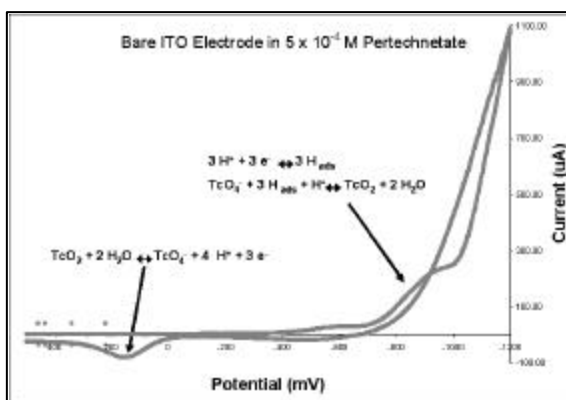


Fig. 1. Cyclic voltammogram of TcO₄⁻ on bare ITO electrode.

they are all nominally attracting TcO_4^- electrostatically by interaction with a quaternary ammonium group. These differences indicate the importance of film choice. Third, the voltammogram has now taken on the look of a quasi-reversible couple for the reduction wave of TcO_4^- by the appearance of a new anodic wave on the reverse scan. The appearance of this new anodic wave (at about -300 mV) is accompanied by a proportionate disappearance of the anodic wave attributed to TcO_2 (at 180 mV). This behavior is clearly seen from the repetitive voltammograms in Figure 3.

Thus the presence of the film has caused a change in mechanism of the reduction of TcO_4^- that is consistent with the formation of a soluble, relatively stable lower oxidation state of Tc, other than the insoluble TcO_2 observed on bare ITO. This change in mechanism is important to our strategy of converting TcO_4^- into a complex for spectroelectrochemical detection. Fourth, the peak heights for both the TcO_4^- reduction wave and this anodic peak are proportional to TcO_4^- concentration, indicating a quantitative response. This is shown in Figure 4, for three concentrations of TcO_4^- at a QPVP- SiO_2 coated electrode. Similar behavior is observed with films containing PDMDAAC and PVTAC.

Interestingly, the reduced Tc slowly forms TcO_2 as a precipitate in the film that scatters light. At high concentration this can even be visualized. Measurement of the absorbance (scattering) of the precipitate by passing light perpendicularly through the film and the substrate ITO showed a linear relationship between concentration of TcO_4^- in the solution to which the electrode was exposed and absorbance and radioactivity from ^{99}Tc by beta counting, which further confirms that TcO_4^- uptake into the film is quantitative, as would be required for sensing.

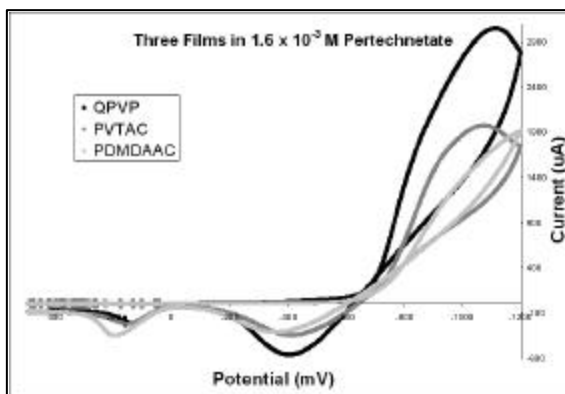


Figure 2. Cyclic voltammogram of TcO_4^- on ITO coated with films with QPVP- SiO_2 , PVA-PVTAC and PDMDAAC- SiO_2 after 30 min of immersion in sample.

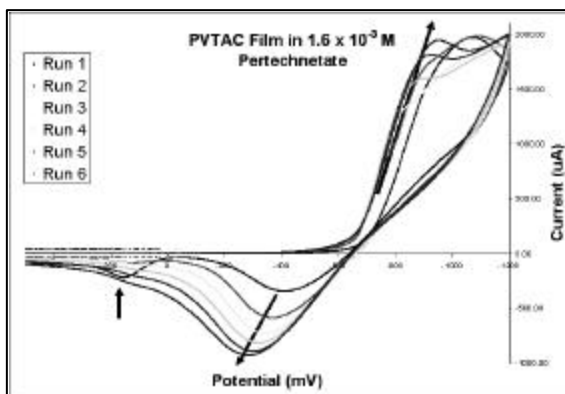


Figure 3. Sequential cyclic voltammograms of TcO_4^- at ITO coated with PVTAC- SiO_2 film after 30 min of immersion in sample.

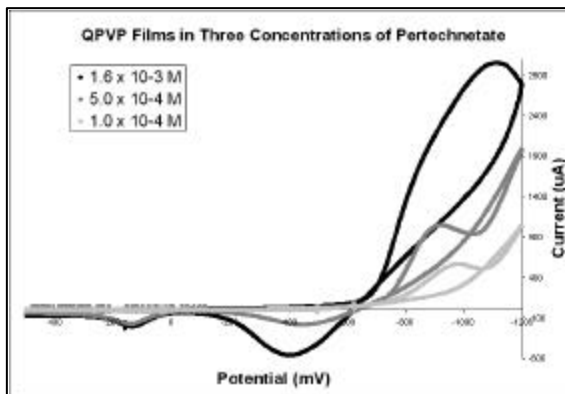


Figure 4. Cyclic voltammograms of three concentrations of TcO_4^- on ITO coated with film of QPVP- SiO_2 after 30 min. of immersion in sample.

CONCLUSIONS

Preliminary evaluation of the ability to preconcentrate the pertechnetate ion in an anion exchange film on an optically transparent electrode has been demonstrated. All three films evaluated were able to show a concentration dependent uptake of pertechnetate. Thus a critical step toward the building of a spectroelectrochemical sensor for pertechnetate has been achieved. The formation of TcO_2 due to irreversible electrochemistry has been shown to be a basis for spectroelectrochemical determination of technetium and has been verified via beta counting.

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